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TECHNICAL REPORT # 3

Introduction

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INTRODUCTION

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This book contains the work of people who spoke and presented posters at the *Ohio Supercomputer Center Workshop on Theory and Applications of Density Functional Theory in Chemisty*, 7-9 May 1990, in Columbus Ohio that was organized by the editors, Jan Labanowski and Jan Andzelm. A large fraction of those attending the conference were people from different corners of chemistry who were simply curious about density functional theory in chemistry, Jan Labanowski being one example. That point was underlined for me shortly before my talk. I was holding a molecular model of what I had assumed would be universally recognized as the icosahedral sixty-carbon-atom Buckminsterfullerene[1] molecule. The person sitting next to me interpreted that model as the rhino virus, a very much larger molecule. As this book demonstrates, there was and is the expectation that density functional methods will enable first principles treatment of chemical systems that are significantly larger and more complex than those accessible by *ab initio* methods.

If the field of computational density functional chemistry is new to you, I thank you for letting your curiosity lead you to read at least a portion of this book. The field is rather new compared to most semiempirical and *ab initio* methods of quantum chemistry. Density functional theory has its origins in solid state physics, and that origin can be traced by simply considering the titles of two related earlier conference proceedings,[2,3] which include work by many of the contributors to this volume. The field has evolved sufficiently to focus exclusively on the chemical aspects of density functional theory now.

In fact, my view of density functional theory has changed almost completely three times in the fifteen years that I have worked in this field. At first I was strongly influenced by John Connolly's assessment of early attempts to improve the first local density functional, $X\alpha$, "When one tries to superimpose subtle corrections on a crude approximation, one is left with a slightly altered, but still crude, approximation".[4] In $X\alpha$ the computationally demanding exchange term of Hartree-Fock is replaced by a computationally less demanding function of the density obtained from consideration of the homogeneous electron gas.[5] If it is viewed as an approximation to Hartree-Fock, $X\alpha$ is indeed a very crude approximation. At

that time I searched for problems that, first, could be treated by density functional theory and, second, for which the intrinsic inaccuracies of density functional theory would not doom the project. Another view of Xα is that it was simply the first local density functional method to be improved by newer local density functionals that are not approximations but direct implementations of the exact Kohn-Sham construction[6] for nondegenerate ground states. In these new methods exact homogeneous electron gas calculations were mapped onto highly degenerate (metallic), noninteracting electron-gas results. These newer local density functionals showed early promise that is reviewed by Salahub, *et al.*, herein and others,[7] but these functionals are not as much of an improvement over the Xα local density functional as they perhaps should be. In the early 1980's I thought that the answer to this puzzle required understanding symmetry-required degeneracy from a density functional point of view, i.e. that density functionals had to be constructed of quantities that are invariant under all the symmetries of the external fields and the density-functional community had to find a consistent way of attaching an irreducible represention label to the density rather than the total wavefunction[8]. Such an understanding is necessary if one wants to follow entirely the breaking of a chemical bond in the case where radicals are formed. On the other hand, a large part of chemistry is concerned with singlet electronic states and potential energy surfaces. Furthermore, as he reviews in this book, Levy formally avoids this degeneracy problem by reformulating density functional theory as a constrained search over all wavefunctions that have the density in question to find the one or more that have the lowest energy as computed by the Schrödinger equation. Although this approach is not computationally advantageous if applied directly, it leads to numerous theorems, which constrain and bound approximate density-functional expressions. Most recently, Becke[9] has chosen to parameterize nonlocal density functionals to atomic data. This new functional of the density and the gradient of the density is quite accurate as demonstrated by the contribution by Ziegler and Tschinke. Results using this and another gradient method are given in contributions by Andzelm, Dixon *et al.*, and Hill *et al.* Gradient methods could be further impro ʲᵘ through the scaling arguments that are also examined by Levy. Currently I want to investigate problems that cannot be treated by density functional theory, such as the avoided crossing of multiple potential energy surfaces discussed herein, and ask why not. Another long-standing problem with local density functionals is their treatment of hydrogen, the atom for which the local density approximation is least appropriate. This problem comes to the fore in treating hydrogen bonding, and example of which is analyzed herein by Hill *et al.*

Having suggested that the most chemically meaningful definition of density functional theory, if it exists at all, is quite time dependent, I will sketch major views of density functional theory in chemistry that currently coexist. Density functional theory is based on the theorem of Hohenberg and Kohn[10] that a functional of the density exists that, when minimized for a given number of electrons and a given external electric potential, gives the ground-state density and energy. Parr and Yang[11] have reviewed how major chemical concepts follow from the existence of such a functional. Some of these concepts are discussed by Méndez and Galván herein. The Hohenberg-Kohn theorem leads to one view of density functional theory which is that it should be pure and thus the ground-state density is the only independent variable of the theory. Pure density functional theories include the Thomas-Fermi method and its extensions.[12] Such a view is sound for molecules, as can be seen by an algorithm described first to me by Connolly (which he credits to E. B. Wilson): Take the ground-state density and integrate it to find the total number of electrons. Find the cusps in the density to locate all nuclei, and then use the cusp condition—that the radial derivative of the density at the cusp is minus twice the nuclear charge times the density at each cusp—to determine the charges on each nucleus.[13] Finally solve Schrödinger's equation for the ground-state density or any other property that is desired. That algorithm was related to me in a very skeptical tone and has been presented in an optimistic tone by Kohn.[14] This algorithm is not a complete implementation of the Hohenberg-Kohn theorem because it does not include all external electric fields and does not directly address variationality. On the other hand, it is applicable to all densities that have some s component on each nucleus, not just the ground-state density. This includes most chemically important densities, and could, in principle, be extended to all densities by also examining the zeros of the density.

If one considers applying density functional theory to excited states orthogonality becomes a problem. Most of the density functional quantum chemical computer codes described in this volume evaluate the kinetic energy quantum-mechanically using one-electron orbitals derived from a local one-electron potential. A local potential, one that when expressed as a function of position is the same for all like-spin one-electron orbitals, need not be a local density functional—local potential methods can treat the Becke correction as demonstrated in the contributions by Ziegler and Tschinke, Andzelm, Dixon *et al.*, and Hill *et al.* In the simplest case of all orbitals being occupied or unoccupied, such a construction solves the orthogonality problem and satisfies the Pauli principle if these orbitals are associated with a single-determinant wavefunction. Kohn and Sham[6] related the ground states calculated by such methods to the Hohenberg-Kohn theorem and

pure density functional theory by mapping the real interacting electronic system of a given ground-state density onto a noninteracting electronic system of the same density. A still less demanding view of density functional theory is that it should be used only to compute all the correlation energy missing from a Hartree-Fock or limited configuration-interaction calculation. This view is represented by Savin in this volume.

All-purpose density functional quantum chemistry was pioneered by Johnson and coworkers from Slater's group in the late 1960's with the advent of the Scattered-Wave computer code for finite systems.[15] (In this volume Wimmer reviews the relationship between local density functional molecular calculations and corresponding band-structure calculations, which are appropriate for periodically infinite systems and for which local density functional methods were developed.) That computer code[16] gets scant mention in this book or elsewhere, because the code requires the user to choose the size of the sphere centered about each atom in which to integrate the local one-electron potential over solid angle in order to obtain an average radial potential. Unfortunately, it was originally assumed that these spheres should touch and not be allowed to overlap. The touching spheres criterion can be met in most, particularly heteronuclear, molecules in a continuum of ways spanning a wide range of total energy. On the other hand, if spheres are allowed to overlap and are chosen to enclose roughly the chemically correct amount of charge, the method becomes much more stable.[17] Perhaps a resurgence of the method will occur if enough readers of this book are influenced by Noodleman, Case, and Baerends through their chapter, which shows that Scattered-Wave calculations compare favorably to calculations using a newer, more precise, but computationally more demanding method. In any event, muffin-tin orbitals provide the preferred starting point for numerious applications in chemistry and physics. One such application is the problem of embedding a cluster into a solid, which is discussed in a chapter by Pisanty, Amador, and Martinez-Carillo.

All of the more recent all-purpose density functional quantum chemistry computer codes replace the muffin-tin approximation which requires only one-dimensional numerical integration with three-dimensional numerical integration of at least the density functional expression for the correlation energy. The first such code[18] is based on similiar band-structure computer code.[19] It uses three-dimensional numerical integration to construct the one-electron secular equation as well as to compute the total energy. Thus any type of orbital basis function can be used. In this volume Delley describes the use of numerical atomic basis functions while Ziegler and Tschinke describe calculations using Slater-type orbitals in current computer codes based on this discrete variational method. The use of numerical basis functions has the advantage that a minimal basis set is exact in the

separated-atom limit within the atomic central-field approximation. On the other hand, there is more collective exprerience throughout quantum chemistry in augmenting Slater-type orbital basis sets. Relativistic discrete-variational calcuations are reviewed by Schneider *et al.* herein. Inspired by *ab initio* Gaussian-type-orbital quantum chemistry computer codes, Sambe and Felton[20] proposed using Gaussian basis functions in local density functional calculations on molecules. Using Gaussian basis functions and fitting the potential to appropriate functional forms lead to a secular equation that can be treated analytically. The total energy in this Gaussian approach becomes numerically stable if the Coulomb potential of the electrons is treated variationally.[21] Extensions and uses of this molecular density-functional method are described in contributions whose first authors are Andzelm, Caldwell, Dixon, Dunlap, Reddington, and Salahub. Pederson and Jackson describe a Gaussian method relying on numerical integration of the secular matrix. In quite detailed fashion, Mintmire tells how to extend the Gaussian approach to helical polymers, using screw symmetry. Results from commercial versions of numerical-basis-set and Gaussian-basis-set molecular local density functional computer codes are compared to each other and *ab initio* results in the contributions by Hill *et al.* and Dixon *et al.*

For me, the most exciting new development in these nonmuffin-tin local density functional methods is the advent of gradients of the total energy using various methods, which are described throughout this volume. The rapid growth in the number of people considering and using density functional methods in chemistry suggests that there are major advances yet to come.

Several times throughout this introduction I have included quite critical statements of John Connolly. These insights have served chemical density functional very well. First, they have taught me and not a few others to be self critical. Second, they perhaps contributed to John Connolly's leaving the field and creating the National Science Foundation supercomputer centers. These centers were in turn a stimulus and example for the formation of the Ohio Supercomputer Center, which hosted this first conference on density functional methods in chemistry.

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